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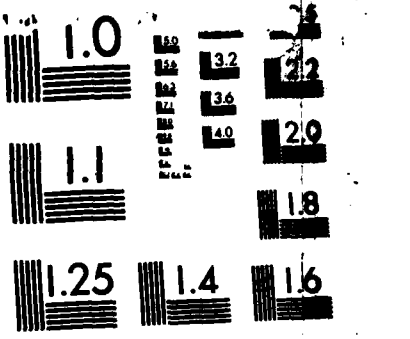

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Picosecond Photoconductivity in Trans-Polyacetylene

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Fast transient photoconductivity measurements of trans-polyacetylene as a function of temperature and photon energy indicate a relatively high quantum efficiency for the photoproduction of mobile, charged, nonlinear excitations. Excitation by a 20ps pulse at 590nm with 10^{15} photons/cm^2 results in a transient photoconductivity of ~0.3 S/cm (at 50 ps) with time scale for decay similar to that measured in picosecond photoinduced absorption experiments. The temperature independence of the fast photoconductivity is interpreted in terms of the photoproduction of "hot" soliton excitations.

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Picosecond Photoconductivity in Trans-Polyacetylene

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Abstract

Fast transient photoconductivity measurements of trans-polyacetylene as a function of temperature and photon energy indicate a relatively high quantum efficiency for the photoproducton of mobile, charged, nonlinear excitations. Excitation by a 20ps pulse at 590nm with 10^{15} photons/cm^2 results in a transient photoconductivity of ≈0.3 S/cm (at 50 ps) with time scale for decay similar to that measured in picosecond photoinduced absorption experiments. The temperature independence of the fast photoconductivity is interpreted in terms of the photoproduction of "hot" soliton excitations.

The possible role of solitons as nonlinear photoexcitations in polyacetylene has received considerable attention[1-4] subsequent to the work of Su and Schrieffer[5], who demonstrated that an electron-hole pair evolves into a soliton-antisoliton pair within 0.1ps after injection onto an isolated trans-$(CH)_x$ chain. Even though their calculation was based on the simple SSH model[6], their predictions were qualitatively confirmed through the experimental observation of the characteristic spectral signatures of solitons in photoinduced absorption[1-4]. Transient photoinduced absorption measurements[1,2] showed the existence of nonlinear shifts in oscillator strength associated with mobile photoexcitations on the time scale predicted by Su and Schrieffer[5]. The one-to-one correspondence between the photoinduced infrared absorptions[3,4] associated with charged[3,4], spinless[7], photoexcitations and the similar features[8] which appear on charge transfer doping indicate the photogeneration of charged solitons.

Orenstein et al[9] questioned the importance of the Su-Schrieffer mechanism and argued that the dominant initial response is the formation of a neutral exciton. In their model, charged solitons are formed only as a by-product after diffusion of a few charged polarons (which result from electrons and holes initially excited on different chains) to the neutral soliton defects already present in the sample. Although the implied decrease in the number of spins was not observed in light induced ESR experiments[7], there is no information on the charged vs neutral excitation branching ratio in the picosecond time regime.

In this letter, we present the results of a comprehensive set of measurements of transient photoconductivity in trans-$(CH)_x$. Excitation by a 20ps pulse at 590 nm with 10^{15} photons/cm^2 results in a transient conductivity of ≈0.3 S/cm (at 50ps) indicative of a relatively high initial quantum efficiency for the fast photoproduction of mobile charged excitations. These mobile charge carriers are produced within picoseconds, consistent with the Su-Schrieffer mechanism. We find that in the sub-nanosecond regime, the photoconductivity and photoinduced absorption are fully consistent; the time decay of the two are similar, and both are essentially temperature (T) independent. We interpret the large, T-independent, picosecond photoconductivity in terms of the photoproduction of "hot" soliton excitations.

The transient photoconductivity, $\sigma_{ph}(t)$, was measured using the Auston switch[10] technique. Each switch consisted of a 50Ω microstrip transmission line (with a 0.2mm gap in the upper conductor) fabricated by vacuum deposition of gold onto an alumina substrate. A thin layer of cis-$(CH)_x$ ($d \approx 0.1$-0.2 μm) was grown across the 0.2mm gap and then isomerized to the trans-structure. The two microstrip contacts were, thus, under the polyacetylene sample which was illuminated from above. In this configuration, $\alpha d \approx 5$, where α^{-1} is the absorption depth.

The microstrip holder was mounted on a cryostat and electrical connections were made to both sides of the line via 0.034 inch stainless coaxial cable (so that temperature could be varied from 300K to 10K). One side of the microstrip was biased with a dc voltage, and the other

side was connected to a PAR model 4400 boxcar system fitted with a Tektronix S-4 sampling head.

A dye laser (PRA model LN105), pumped by a nitrogen laser operated at 8 Hz, was used to produce 20ps pulses of up to 20μJ/pulse. Photon energies could be varied from 1.4 to 2.9 eV. The boxcar was triggered with the light pulse (via a photodiode) in order to eliminate jitter. On alternate pulses, the beam was blocked and the baseline sampled so that the effects of sampling head drift and coherent pickup could be minimized. The photoresponse was signal averaged to increase the signal-to-noise ratio. Steady state measurements were carried out with the same samples described above. In this case, the light was from a tungston lamp through a monochromator; the beam was chopped (14 Hz) and lock-in detection was used to measure the voltage drop across a 1M resistor in series with the sample.

All measurements reported in this letter were obtained with uniform illumination of the sample across the 0.2mm gap. Within experimental error, the magnitude of the transient photocurrent was linearly proportional to the energy of the laser pulse and to the applied bias voltage, implying that the contacts were ohmic and that dielectric relaxation effects were not important[10]. In cases where the illumination was not uniform (i.e. the laser focused to a size smaller than the gap) charging effects were observed, particularly at low temperatures where the dark resistance was extremely high.

Figure 1 shows the transient photoconductivity due to a 1μJ pulse at 2.1 eV, with a bias voltage of 300V. The rise time of the

signal is ≈50ps. The observed rise time represents a convolution of the sampling head response time (25ps), the laser pulse rise time (15ps), the trigger jitter (15ps), the rise time of the transmission line, and the rise time of the photocurrent. Thus, the charge carriers are produced within picoseconds of optical excitation. The fast rise is followed by (approximately exponential) decay with a time constant of ≈300ps; the ratio of the photocurrent at 1500 ps to that at 50ps is 0.03. The experimental demonstration that the photoconductivity and the photoinduced change in optical absorption[1,2], $\delta\alpha(t)$, decay on the same time scale implies that the photogenerated charge carriers involve a major shift in oscillator strength, consistent with the proposed photogeneration of charged solitons.

The magnitude of σ_{ph} is large. For an absorbed photon flux of 10^{15} cm^{-2} per pulse, the photocurrent (at ≈50ps) is 4×10^{-4}A (i.e. current density $\approx10^{3}$ A/cm^{2}) with good reproducibility from sample to sample. This corresponds to a conductivity of about 0.3 S/cm with a possible error of a factor of two due to uncertainty in αd in the top-illumination measurement geometry. The increase in σ_{ph} over the dark room temperature value is five to six orders of magnitude!

Waveforms obtained with other photon energies were identical to Fig.1, but with different amplitudes. Figure 2 shows the amplitude of the 50ps photocurrent as a function of photon energy. Also plotted in Fig. 2 is the magnitude of the steady state photocurrent (on the same

sample) as a function of photon energy. The shapes of the two excitation profiles are similar, differing only at higher photon energies where the fast photoconductivity is essentially independent of $\hbar\omega$. Note, however, that the magnitude of the steady state response is many orders of magnitude smaller. The close agreement between the photon energies at which absorption and photoconductivity onset is indicative of an interband transition (in contrast to a neutral exciton). Although the long wavelength exponential tail ($\hbar\omega<E_g$) may be due to direct photoproduction of solitons[3,11], excitation at $\hbar\omega>1.5$ eV involves an interband transition (free electron-hole pair) as the initial step.

In the process of carrying out the steady state measurements, we re-examined the decay of the photocurrent in the long time regime from 10^{-6} to 10^{-3} seconds. In contrast to the report of Yacobi et al[12], the results reconfirmed the long tail with current falling as $t^{-0.65}$ (dispersive hopping transport) as reported by Etemad et al[11].

The shape of $\sigma_{ph}(t)$ is temperature independent (in the sub-nanosecond regime) from 10K to 300K, indicating a temperature independent decay mechanism. The temperature dependences of the (normalized) magnitudes of the transient (50ps) and steady state photoconductivities are shown in Figure 3. The magnitude of the transient response is also temperature independent, whereas the steady state photocurrent is strongly temperature dependent with a thermal activation energy of about 0.2 eV.

The relationship between the photocurrent and the incident photon flux is given by

$$\sigma_{ph} = (E/\hbar\omega)e\eta\varphi\mu \qquad (1)$$

where $(E/\hbar\omega)$ is the number of absorbed photons, η is the quantum efficiency, φ is the probability to escape geminate (or early time) recombination, and μ is the mobility. Using $\sigma_{ph}(50ps)\approx 0.3$ S/cm and assuming both that $\eta=1$ and that all the initial carriers live to at least 50ps ($\varphi=1$), the calculated mobility would be $\mu \approx 10^{-2}$ cm^2/v-s. However, the picosecond[1,2] and sub-picosecond[13] $\delta\alpha(t)$ data indicate that the number of photoexcitations has already decayed to less than 10^{-2} of the initial value at 50ps. Thus, the carrier yield at 50ps is $\varphi\approx 0.01$. Using this value for φ in eqn 1 results in a mobility of approximately 1cm^2/V-s. With this value, the net distance drifted in the measured decay time (300ps) is about 400Å, in good agreement with that inferred from the picosecond decay of the photoinduced dichroism[1].

The photoconductivity results, therefore, indicate a relatively high initial quantum efficiency for the fast photoproduction of charged nonlinear excitations, consistent with the Su-Schrieffer mechanism. Although the branching ratio of charged to neutral excitations has not been measured, the close agreement between the spectral onset of absorption and high η photoconductivity is traditionally interpreted as ruling out the generation of neutral excitons as the <u>primary</u> excitations. We conclude therefore that the photoinduced absorption at 1.4 eV, due to neutral excitations[4], is generated as a secondary process during the

rapid initial recombination of the photoinduced charged excitations. This conclusion is consistent with the faster decay[13b] of $\delta\alpha(t)$ at 0.8eV (in the "mid-gap" absorption due to charged species) than at 1.5eV.

Since the photoinduced absorption is sensitive only to the number of nonlinear photoexcitations (and not their mobility), the agreement between the time scales for decay of $\sigma_{ph}(t)$ and $\delta\alpha(t)$ implies that the decay of photocurrent is due primarily to decay of the number of charge carriers. Thus, trapping or ballistic acceleration to the chain ends are ruled out as major processes on this time scale. A small number of photocarriers are trapped, however, and survive the $t<10^{-9}$s recombination as evidenced by the residual weak photoinduced absorption[3,4] and weak dispersive transport photoconductivity[11] observed for $t>10^{-6}$s .

The temperature independence of the picosecond photoconductivity is of particular importance; it indicates that the recombination processes and the mobility of the charged nonlinear excitations are T-independent. This insensitivity to the ambient temperature implies that the carriers are "hot". The photogeneration of such "hot" carriers is consistent with the excitation of soliton-antisoliton pairs. In this mechanism, the initial electron-hole pairs with energy $\hbar\omega>E_g$ rapidly begin to thermalize toward the band edge by phonon emission[14]. However, as the soliton-like distortions begin to form, the solitons and phonons would be expected to decouple leaving a large fraction of the excess energy, $\delta E = E_g-(4/\pi)\Delta$, in the soliton system. Although initially these solitons will rapidly lose energy through phonon emission,

this process becomes inefficient at velocities below the sound velocity[15]. Thus, the mobility and recombination of the resulting charged "hot" soliton photoexcitations would be insensitive to the temperature of the sample. The temperature independence of the fast photoconductivity, therefore, provides the first evidence of the robust features expected for such stable nonlinear excitations[16].

The existence of these fast nonlinear processes is not only important as confirmation of the proposed mechanism for the photogeneration of charged solitons, but also establishes this class of conjugated polymers as extremely fast nonlinear optical materials with relatively large third-order susceptibilities[17]. These potentially important nonlinear optical properties arise directly from the shifts in oscillator strength which result from the novel nonlinear photo-excitations (solitons in the case of a degenerate ground state, and polarons or bipolarons when the ground state degeneracy is lifted[18]).

In conclusion, we have investigated the fast transient photoconductivity of trans-polyacetylene as a function of temperature and photon energy. The results indicate a relatively high initial quantum efficiency for the fast photoproduction of mobile, charged, nonlinear excitations and are thus consistent with the Su-Schrieffer mechanism for the photoproduction of charged solitons. The agreement between the spectral onset of absorption and high quantum efficiency photo-conductivity implies that the optical absorption is due to an interband transition (in contrast to a neutral exciton). We therefore conclude that the photoinduced absorption at 1.4eV, due to neutral excitations, is

generated as a secondary process during the rapid initial recombination of the photoinduced charged excitations. The temperature independence of the picosecond photoconductivity is interpreted as evidence of the photoproduction of "hot" solitons.

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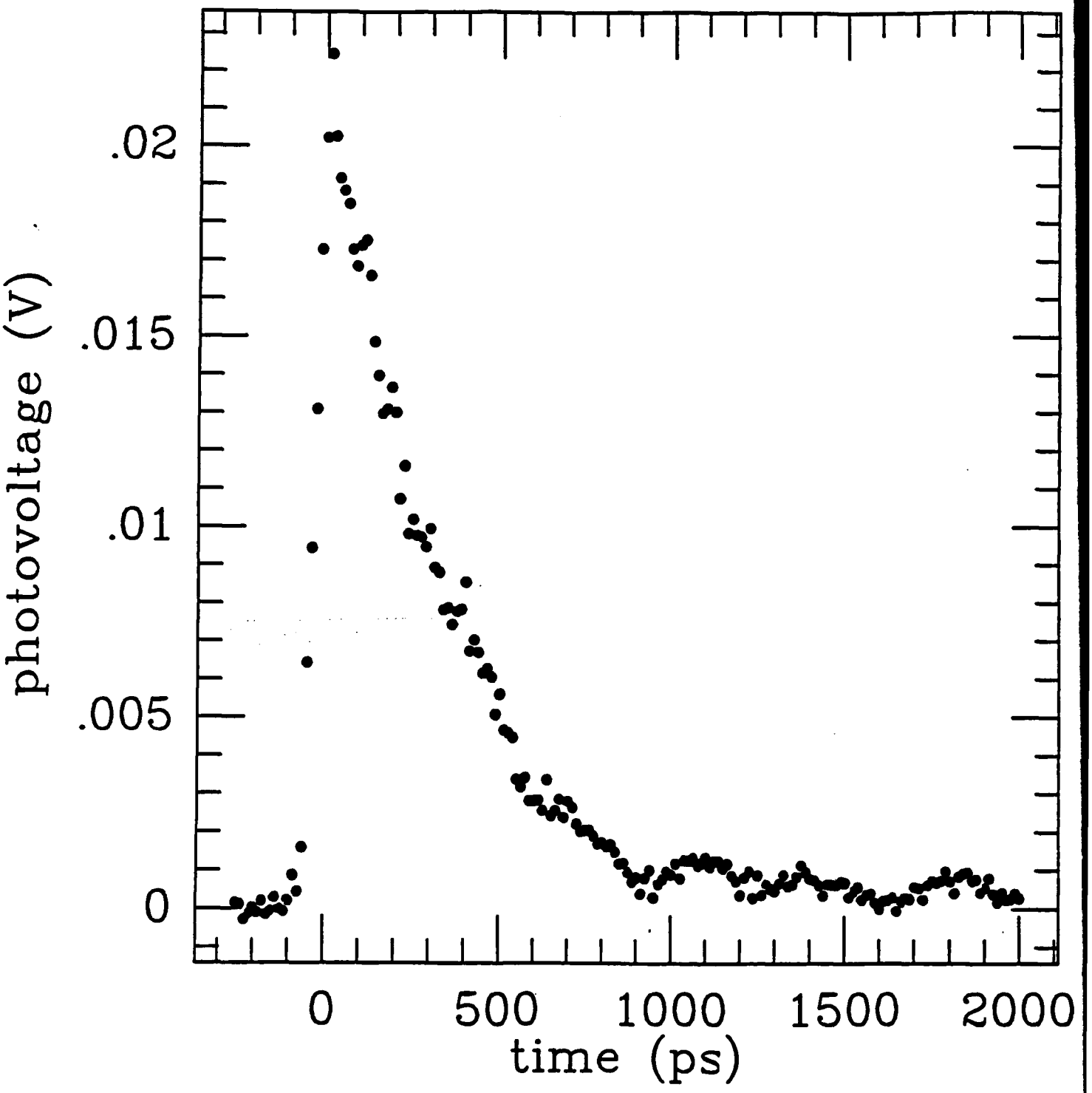
Figure Captions:

Figure 1: Transient photovoltage (across 50Ω) of trans-$(CH)_x$ in the Auston switch configuration (see text).

Figure 2: Excitation profile of the photoconductivity; ooo,steady state at 300K; ΔΔΔ, pulsed at 300k; and ◇◇◇,pulsed at 80K.

Figure 3: Temperature dependence of the magnitude of σ_{ph}: steady state (Δ ; excited at 500nm) and picosecond (◇ ; excited at 590nm. The solid line emphasizes the T-independence of the fast photoconductivity.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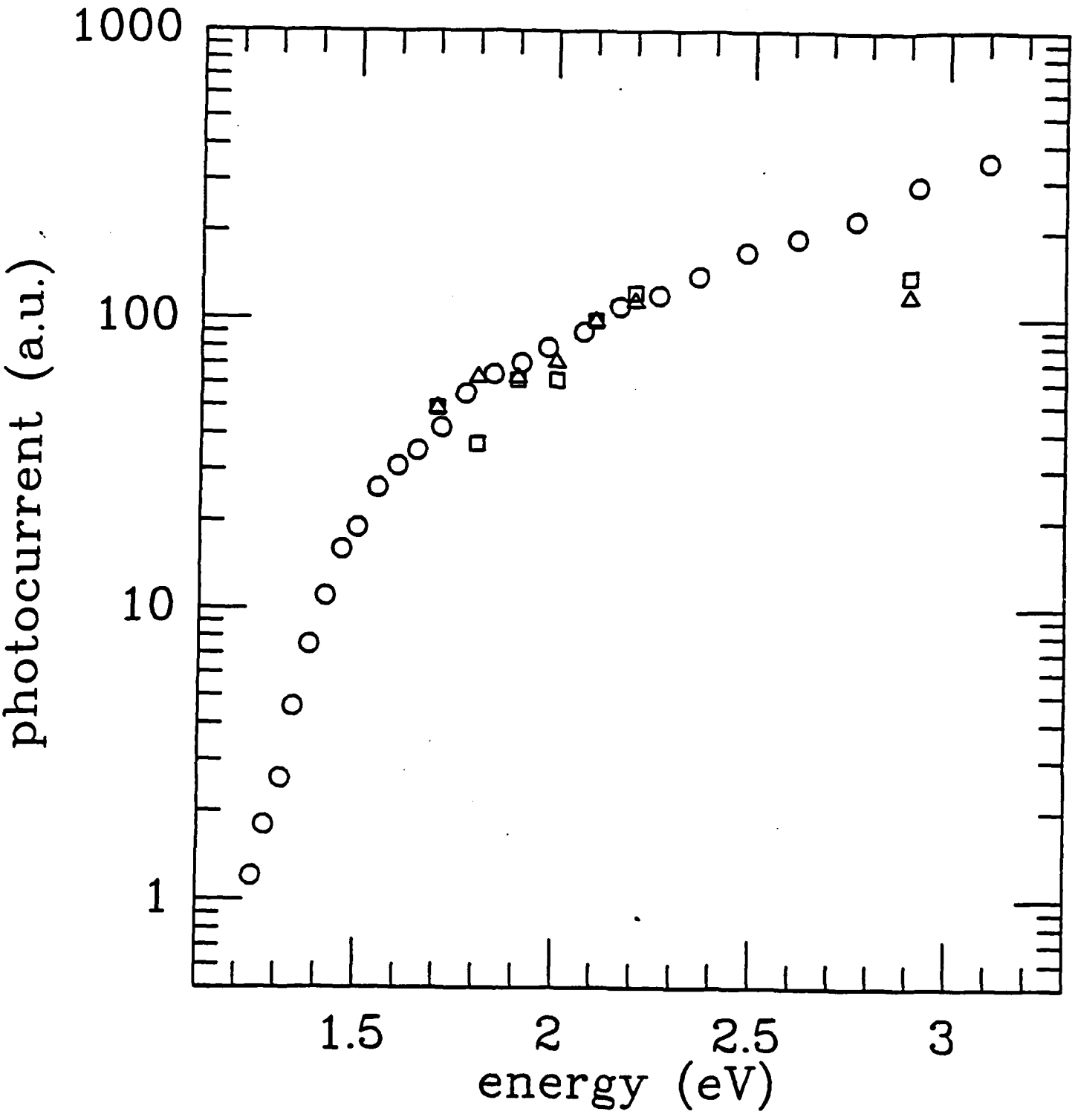
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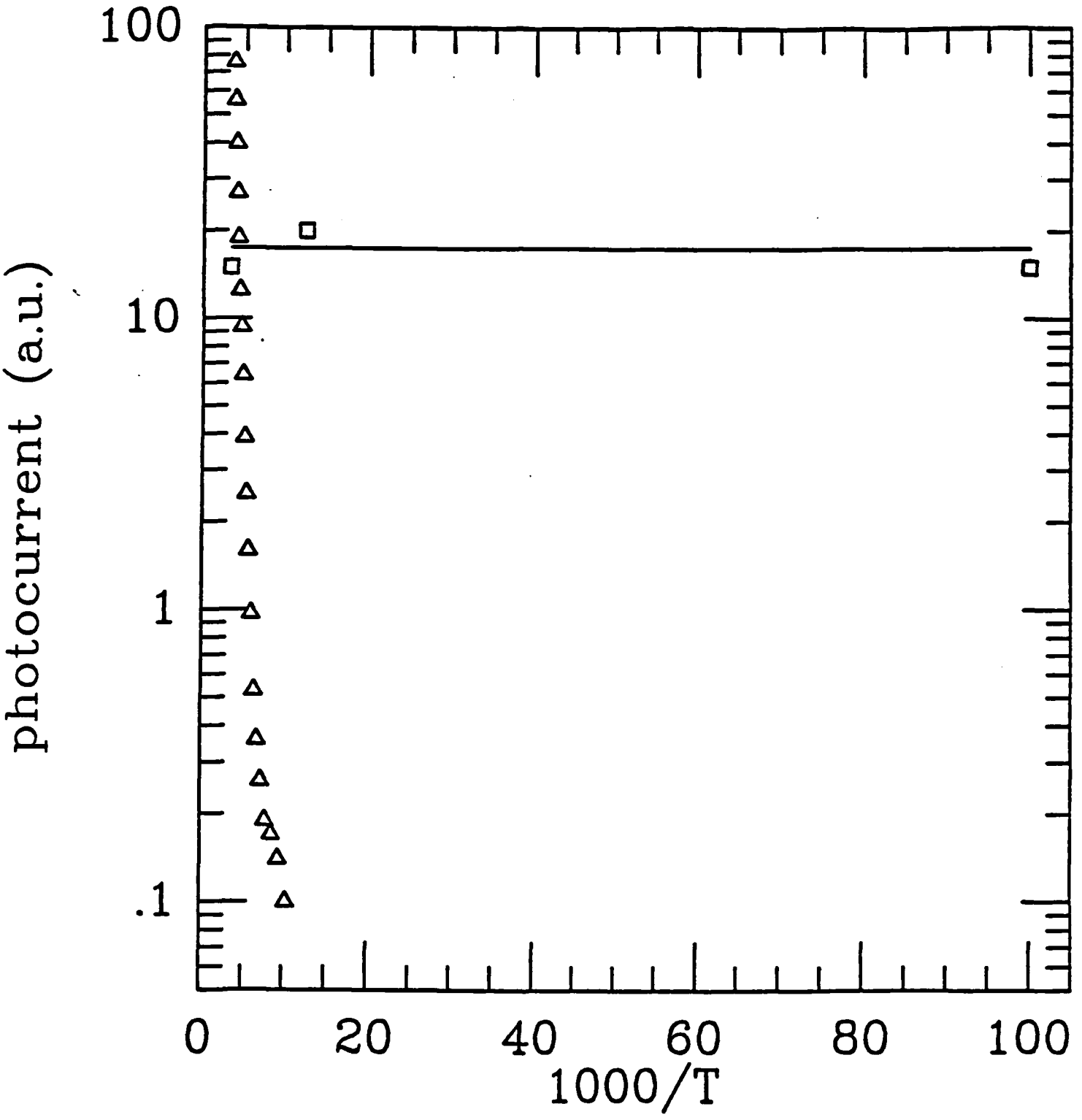
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